

What is claimed is:**1. A method of curing**

a composition comprising

- (a) at least one free-radical-polymerisable compound or
- (b) at least one compound that, under the action of an acid, is able to enter into a polymerisation, polycondensation or polyaddition reaction, or
- (c) at least one compound that, under the action of a base, is able to enter into a polymerisation, polycondensation or polyaddition reaction, or

a mixture of components (a) and (b), or

a mixture of components (a) and (c); and

- (d) at least one photolabile compound that is activatable by plasma discharge;

wherein

the composition is applied to a three-dimensional substrate and

the curing is carried out in a plasma discharge chamber.

2. A method of curing

a composition comprising

- (a) at least one free-radical-polymerisable compound or
- (b) at least one compound that, under the action of an acid, is able to enter into a polymerisation, polycondensation or polyaddition reaction, or
- (c) at least one compound that, under the action of a base, is able to enter into a polymerisation, polycondensation or polyaddition reaction, or

a mixture of components (a) and (b), or

a mixture of components (a) and (c);

- (d) at least one photolabile compound that is activatable by plasma discharge; and

- (e) at least one light stabiliser compound or UV absorber compound;

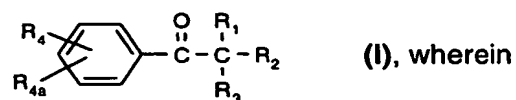
wherein

the curing is carried out in a plasma discharge chamber.

3. A method according to either claim 1 or claim 2, wherein component (d) in the composition is a free-radical photoinitiator, a photolabile acid or a photolabile base.

4. A method according to either claim 1 or claim 2, wherein component (d) in the composition is at least one compound selected from the group of benzophenones, benzophenone derivatives, acetophenone, acetophenone derivatives, halomethylbenzophenones, halomethylarylsulfones, dialkoxyacetophenones, anthracene, anthracene derivatives, thioxanthone, thioxanthone derivatives, 3-ketocoumarin, 3-ketocoumarin derivatives, anthraquinone, anthraquinone derivatives, α -hydroxy- or α -amino-acetophenone derivatives, α -sulfonylacetophenone derivatives, 4-aroyl-1,3-dioxolanes, benzoin alkyl ethers and benzilketals, phenyl glyoxalates and derivatives thereof, dimeric phenyl glyoxalates, peresters, monoacylphosphine oxides, bisacylphosphine oxides, trisacylphosphine oxides, halomethyltriazines, titanocenes, borate compounds, O-acyloxime compounds, camphorquinone derivatives, iodonium salts, sulfonium salts, iron aryl complexes, oximesulfonic acid esters and photolabile amines.

5. A method according to either claim 1 or claim 2, wherein component (d) in the composition is at least one compound of formula I, II, III or/and IV



R₁ is C₁-C₁₂alkyl or C₁-C₁₂alkoxy;

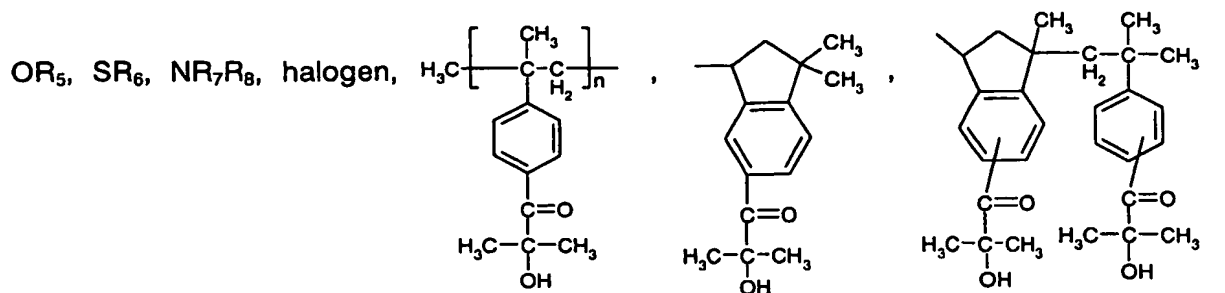
R₂ is phenyl, OR₅ or NR₇R₈;

R₃ has one of the definitions given for R₁ or is C₃-C₁₂alkenyl, phenyl-C₁-C₆alkyl or C₁-C₆alkylphenyl-C₁-C₆alkyl;

or R₁ and R₃, together with the carbon atom to which they are bonded, form a cyclohexyl ring;

R₂ being phenyl when R₁ and R₃ are both alkoxy;

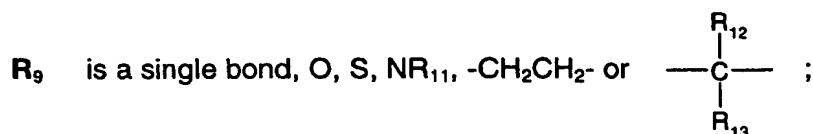
R_4 and R_{4a} are each independently of the other hydrogen, C_1 - C_{12} alkyl, C_1 - C_{12} hydroxyalkyl,



n is a number from 1 to 10;

R_5 and R_6 are each independently of the other hydrogen, C_1 - C_{12} alkyl, C_1 - C_{12} alkenyl, phenyl, benzyl, $Si(CH_3)_3$ or $-[C_aH_{2a}X]_b-R_{10}$;

R_7 and R_8 are each independently of the other hydrogen, C_1 - C_{12} alkyl or C_2 - C_5 hydroxyalkyl, or R_7 and R_8 , together with the N atom to which they are bonded, form a 5- or 6-membered ring, which may also contain O atoms or a NR_{11} group;



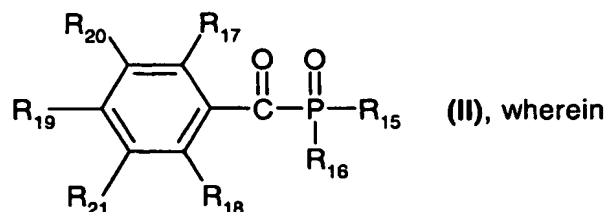
a and b are each independently of the other a number from 1 to 12;

X is S, O or NR_{11} ;



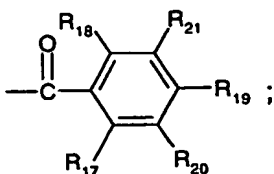
R_{11} is hydrogen, phenyl, phenyl- C_1 - C_4 alkyl, C_1 - C_{12} alkyl or C_2 - C_5 hydroxyalkyl; and

R_{12} , R_{13} and R_{14} are each independently of the others hydrogen or methyl;



R_{15} and R_{16} are each independently of the other C_1 - C_{12} alkyl, C_1 - C_{12} alkoxy; phenyl which is unsubstituted or substituted by one or more OR_{22} , SR_{23} , $NR_{24}R_{25}$, C_1 - C_{12} alkyl or halogen

substituents; or R_{15} and R_{16} are biphenyl, naphthyl, phenyl- C_1 - C_4 alkyl or

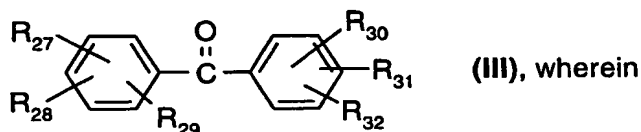


R_{17} and R_{18} are each independently of the other C_1 - C_{12} alkyl, C_1 - C_{12} alkoxy, CF_3 or halogen;

R_{19} , R_{20} and R_{21} are each independently of the others hydrogen, C_1 - C_{12} alkyl, C_1 - C_{12} alkoxy, CF_3 or halogen;

R_{22} , R_{23} , R_{24} and R_{25} are each independently of the others hydrogen, C_1 - C_{12} alkyl, C_2 - C_{12} -alkenyl, C_3 - C_8 cycloalkyl, phenyl, benzyl, or C_2 - C_{20} alkyl which is interrupted by O atoms and is unsubstituted or substituted by OH or/and SH; or R_{24} and R_{25} , together with the N atom to which they are bonded, form a 5- or 6-membered ring, which may also contain O or S atoms or an NR_{26} group; and

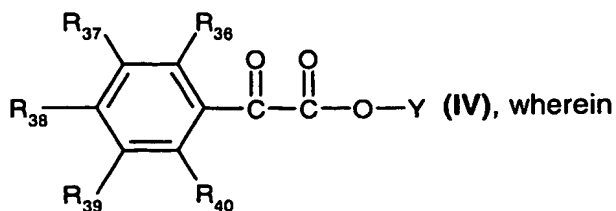
R_{26} is hydrogen, phenyl, phenyl- C_1 - C_4 alkyl, C_1 - C_{12} alkoxy, C_1 - C_{12} alkyl or C_1 - C_{12} hydroxyalkyl;



R_{27} , R_{28} , R_{29} , R_{30} , R_{31} and R_{32} are each independently of the others hydrogen, C_1 - C_4 alkyl, phenyl, naphthyl, $-OR_{35}$, $-SR_{35}$, $-(CO)O(C_1$ - C_4 alkyl), halogen, $NR_{33}R_{34}$ or a monovalent linear or branched siloxane radical, or R_{29} and R_{30} , each in the o-position to the carbonyl group, together form a S atom; and

R_{33} and R_{34} are each independently of the other hydrogen, C_1 - C_4 alkyl, C_2 - C_6 hydroxyalkyl, or R_{33} and R_{34} , together with the N atom to which they are bonded, form a 5- or 6-membered ring, which may also contain O atoms or a NR_{11} group; and

R_{35} is C_1 - C_{12} alkyl, C_2 - C_6 hydroxyalkyl or phenyl;



R_{36} , R_{37} , R_{38} , R_{39} and R_{40} are each independently of the others hydrogen, C_1 - C_{12} alkyl unsubstituted or substituted by OH, C_1 - C_4 alkoxy, phenyl, naphthyl, halogen, CN and/or by $-OCOR_{41}$, or C_2 - C_{12} alkyl which is interrupted by one or more O atoms, or R_{36} , R_{37} , R_{38} , R_{39}

and R_{40} are OR_{42} , SR_{43} , $NR_{44}R_{45}$, halogen, a monovalent linear or branched siloxane radical, or phenyl unsubstituted or substituted by one or two C_1 - C_4 alkyl or/and one or two C_1 - C_4 -alkoxy substituents, it being possible for the substituents OR_{42} , SR_{43} , $NR_{44}R_{45}$ to form 5- or 6-membered rings by way of the radicals R_{42} , R_{43} , R_{44} and/or R_{45} with further substituents on the phenyl ring or with one of the carbon atoms of the phenyl ring;

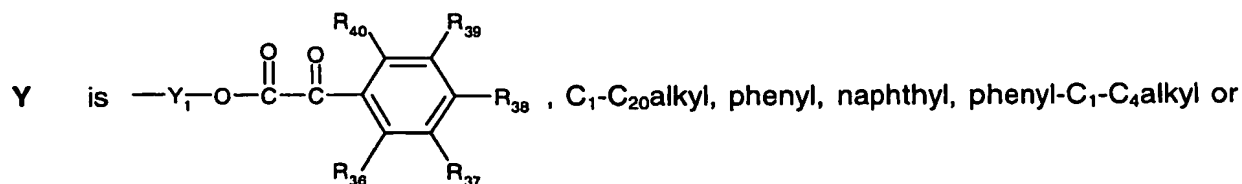
R_{41} is C_1 - C_8 alkyl, or phenyl unsubstituted or substituted by from one to three C_1 - C_4 alkyl and/or one to three C_1 - C_4 alkoxy substituents;

R_{42} and R_{43} are each independently of the other hydrogen, C_1 - C_{12} alkyl unsubstituted or substituted by OH, C_1 - C_4 alkoxy, phenyl, phenoxy or/and by $-OCOR_{41}$, or C_2 - C_{12} alkyl which is interrupted by one or more O atoms, or R_{42} and R_{43} are phenyl unsubstituted or substituted by C_1 - C_4 alkoxy, phenyl or/and by C_1 - C_4 alkyl, or R_{42} and R_{43} are C_3 - C_6 alkenyl, cyclopentyl, cyclohexyl or naphthyl;

R_{44} and R_{45} are each independently of the other hydrogen, C_1 - C_{12} alkyl unsubstituted or substituted by OH, C_1 - C_4 alkoxy or/and by phenyl, or C_2 - C_{12} alkyl which is interrupted by one or more O atoms, or R_{44} and R_{45} are phenyl, $-COR_{41}$ or SO_2R_{46} , or R_{44} and R_{45} , together with the nitrogen atom to which they are bonded, form a 5-, 6- or 7-membered ring, which may also be interrupted by $-O-$ or $-NR_{47}-$;

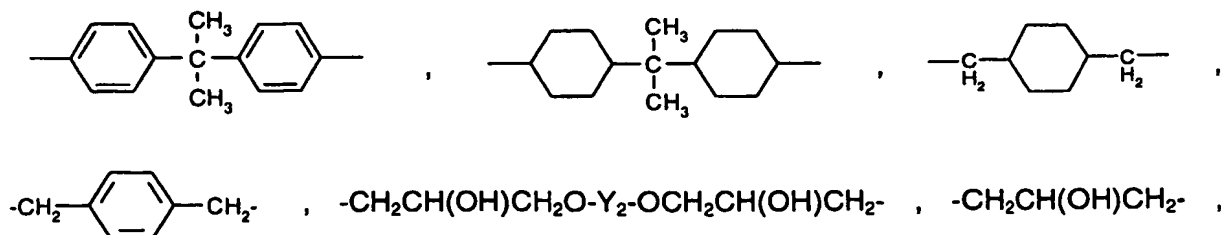
R_{46} is C_1 - C_{12} alkyl, phenyl or 4-methylphenyl;

R_{47} is hydrogen, C_1 - C_8 alkyl unsubstituted or substituted by OH or by C_1 - C_4 alkoxy, or is phenyl unsubstituted or substituted by OH, C_1 - C_4 alkyl or by C_1 - C_4 alkoxy;

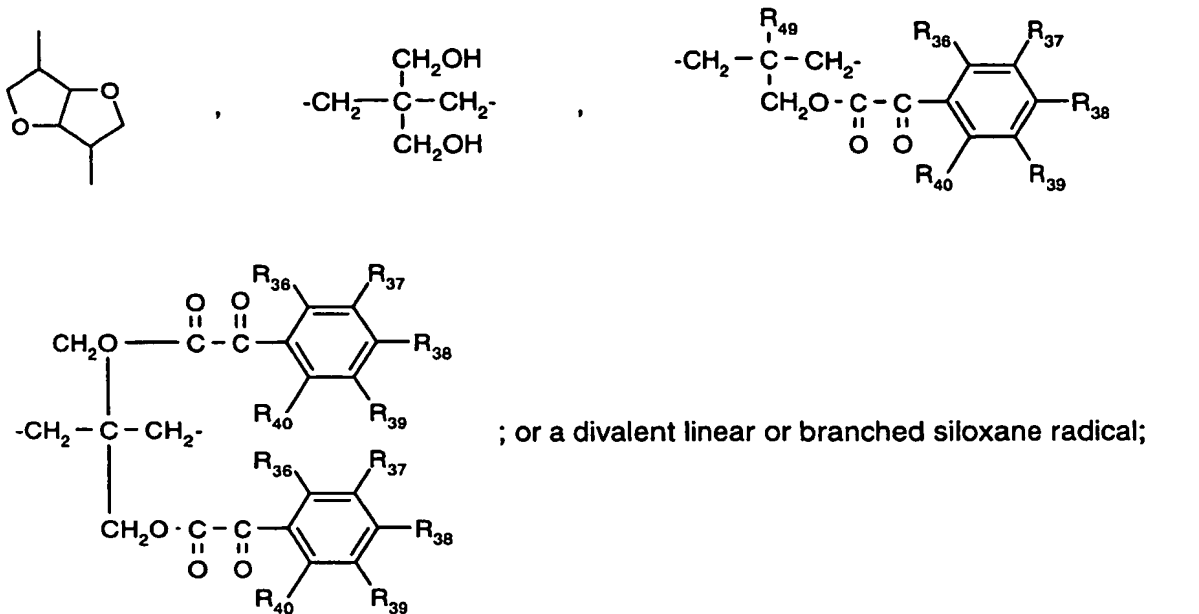


a monovalent linear or branched siloxane radical;

Y_1 is C_1 - C_{12} alkylene, C_4 - C_8 alkenylene, C_4 - C_8 alkynylene, cyclohexylene, C_4 - C_{40} alkylene interrupted by one or more $-O-$, $-S-$ or $-NR_{48}-$, or is phenylene or Y_1 is a group



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Y₂ has the same definitions as **Y₁** with the exception of the formula

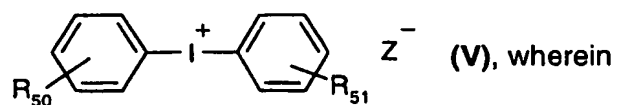
$-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}-\text{Y}_2-\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2-$;

R₄₈ is hydrogen, C₁-C₁₂alkyl or phenyl; and

R₄₉ is hydrogen, CH₂OH or C₁-C₄alkyl.

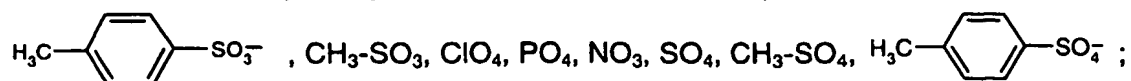
6. A method according to claim 4, wherein component (d) in the composition is at least one compound of formula I or/and II, especially a mixture of a compound of formula I and a compound of formula II.

7. A method according to either claim 1 or claim 2, wherein component (d) in the composition is at least one compound of formula V, VI, VII or/and VIIa

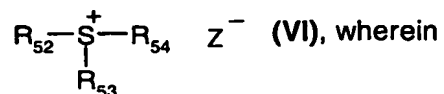


R₅₀ and **R₅₁** are each independently of the other hydrogen, C₁-C₂₀alkyl, C₁-C₂₀alkoxy, OH-substituted C₁-C₂₀alkoxy, halogen, C₂-C₁₂alkenyl, cycloalkyl, especially methyl, isopropyl or isobutyl; and

Z is an anion, especially PF₆, SbF₆, AsF₆, BF₄, (C₆F₅)₄B, Cl, Br, HSO₄, CF₃-SO₃, F-SO₃,

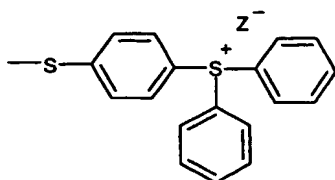


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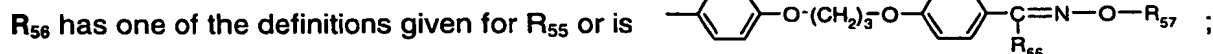
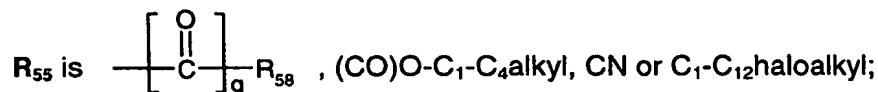
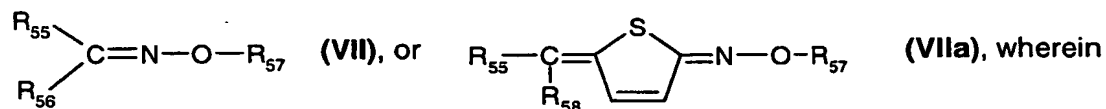


R_{52} , R_{53} and R_{54} are each independently of the others unsubstituted phenyl, or phenyl sub-

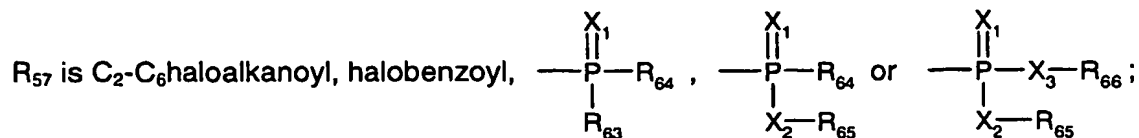
stituted by -S-phenyl or by



Z is as defined above;



R_{57} is C_1 - C_{18} alkylsulfonyl, C_1 - C_{10} haloalkylsulfonyl, camphorylsulfonyl, phenyl- C_1 - C_3 alkylsulfonyl, C_3 - C_{30} cycloalkylsulfonyl, phenylsulfonyl, naphthylsulfonyl, anthracylsulfonyl or phenanthrylsulfonyl, the groups cycloalkyl, phenyl, naphthyl, anthracyl and phenanthryl of the radicals C_3 - C_{30} cycloalkylsulfonyl, phenyl- C_1 - C_3 alkylsulfonyl, phenylsulfonyl, naphthylsulfonyl, anthracylsulfonyl and phenanthrylsulfonyl being unsubstituted or substituted by one or more halogen, C_1 - C_4 haloalkyl, CN, NO_2 , C_1 - C_{16} alkyl, phenyl, C_1 - C_4 alkylthio, C_1 - C_4 alkoxy, phenoxy, C_1 - C_4 alkyl-O(CO)-, C_1 - C_4 alkyl-(CO)O-, $R_{67}OSO_2$ - and/or $-NR_{60}R_{61}$ substituents; or



X_1 , X_2 and X_3 are each independently of the others O or S;

q is 0 or 2; and

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R₅₈ is C₁-C₁₂alkyl, cyclohexyl, camphoryl, unsubstituted phenyl, or phenyl substituted by one or more halogen, C₁-C₁₂alkyl, OR₅₉, SR₅₉ or NR₆₀R₆₁ substituents;

R₅₉ is C₁-C₁₂alkyl, phenyl, phenyl-C₁-C₄alkyl or C₁-C₁₂hydroxyalkyl;

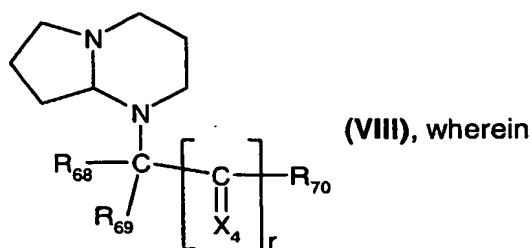
R₆₀ and **R₆₁** are each independently of the other hydrogen, C₁-C₄alkyl, C₂-C₆hydroxyalkyl, or **R₆₀** and **R₆₁**, together with the N atom to which they are bonded, form a 5- or 6-membered ring, which may also contain O atoms or an NR₆₂ group;

R₆₂ is hydrogen, phenyl, phenyl-C₁-C₄alkyl, C₁-C₁₂alkyl or C₂-C₅hydroxyalkyl;

R₆₃, **R₆₄**, **R₆₅** and **R₆₆** are each independently of the others C₁-C₆alkyl, C₁-C₆haloalkyl; or phenyl unsubstituted or substituted by C₁-C₄alkyl or by halogen; and

R₆₇ is hydrogen, C₁-C₄alkyl, phenyl or tolyl.

8. A method according to either claim 1 or claim 2, wherein component (d) in the composition is at least one compound of formula VIII



r is 0 or 1;

X₄ is CH₂ or O;

R₆₈ and **R₆₉** are each independently of the other hydrogen or C₁-C₂₀alkyl; and

R₇₀ is unsubstituted or C₁-C₁₂alkyl- or C₁-C₁₂alkoxy-substituted phenyl, naphthyl or biphenyl.

9. A method according to either claim 1 or claim 2, wherein the composition comprises, in addition to the photolabile component (d), other additives (h), sensitizer compounds (f) or/and dyes or pigments (g).

10. A method according to claim 1, wherein the composition comprises at least one light stabiliser or/and at least one UV absorber compound.

11. A method according to either claim 1 or claim 2, wherein the composition is a surface coating.

12. A method according to either claim 1 or claim 2, wherein the composition is a printing ink.
13. A method according to either claim 1 or claim 2, wherein the composition comprises as polymerisable component solely free-radical-polymerisable compounds (a).
14. A method according to claim 13, wherein the free-radical-polymerisable compound comprises at least one mono-, di-, tri- or tetra-functional acrylate monomer and/or at least one mono-, di-, tri- or tetra-functional acrylate-functional oligomer.
15. A method according to either claim 1 or claim 2, wherein the composition comprises as polymerisable component solely cationically polymerisable or crosslinkable compounds (b).
16. A method according to either claim 1 or claim 2, wherein the composition comprises as polymerisable component a mixture of at least one free-radical-polymerisable compound (a) and at least one cationically polymerisable compound (b).
17. A coated substrate which is coated on at least one surface by means of the method according to either claim 1 or claim 2.
18. A coating obtainable by a method according to either claim 1 or claim 2.
19. A method of curing
a composition comprising
- (1) a combination of at least one electron acceptor compound, especially a maleimide compound, and at least one electron donor compound, especially a vinyl ether compound; and
 - (2) optionally at least one free-radical-polymerisable compound (a),
- wherein the curing is carried out in a plasma discharge chamber.
20. A method of curing
a composition comprising

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(a) at least one free-radical-polymerisable component having at least one ethylenically unsaturated double bond, the free-radical-polymerisable component optionally additionally being functionalised with OH, NH₂, COOH, epoxy or NCO groups; and

(a1) at least one polyacrylate or/and polyester polyol in combination with melamine or with a melamine derivative, or in combination with a blocked or non-blocked polyisocyanate; or

(a2) at least one carboxyl-, anhydride- or amino-functional polyester or/and at least one carboxyl-, anhydride- or amino-functional polyacrylate in combination with an epoxy-functional polyester or polyacrylate; or

(a3) a mixture of (a1) and (a2);

(d) at least one photolabile compound that is activatable by plasma discharge;

wherein

the curing of the composition is carried out in a plasma discharge chamber and, optionally, thermal pre- or after-treatment is carried out.

21. A method of producing mouldings from composite materials, wherein a support is impregnated with a composition comprising

(a) at least one free-radical-polymerisable compound or

(b) at least one compound that, under the action of an acid, is able to enter into a polymerisation, polycondensation or polyaddition reaction, or

(c) at least one compound that, under the action of a base, is able to enter into a polymerisation, polycondensation or polyaddition reaction, or

a mixture of components (a) and (b), or

a mixture of components (a) and (c); and

(d) at least one photolabile compound that is activatable by plasma discharge;

and is introduced into a mould;

wherein the curing is carried out in a plasma discharge chamber and, optionally, thermal aftertreatment is carried out.